

OXIDATION OF AROMATIC COMPOUNDS WITH UV RADIATION/OZONE/HYDROGEN PEROXIDE

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ABSTRACT:

A large variety of organic and inorganic compounds may be found in wastewater. Among these compounds, aromatics are characterized by their high toxicity and very low degradability by conventional treatments.

This paper presents the results of an investigation about the oxidation of two substituted benzenes in a semi-batch reactor. Phenol, substituted with an electron-donating group (-OH), and benzoic acid substituted with an electron-withdrawing group (-COOH). The advanced oxidation processes studied were UV, ozone, hydrogen peroxide and its combinations. The pH dependence and the influence of the initial concentration of hydrogen peroxide were studied to find the optimal conditions for a complete and fast oxidation of both compounds.

Experimental results indicated that both phenol and benzoic acid are destroyed more rapidly by ozone at higher pH (9-12), while ozonation combined with hydrogen peroxide or/and UV is considerably faster at low pH (3-7).

KEYWORDS:

Wastewater, phenol, benzoic acid, ozone, UV, hydrogen peroxide, ·OH radical.

INTRODUCTION:

Advanced oxidation processes involving hydroxyl radicals ·OH, represent a new treatment concept and have gained increasing interest in treatment of industrial and drinking wastewater to remove organic and inorganic contaminants. The common target of many groups working worldwide is to increase the number of applications of these processes and to improve their efficiency.

Ozonation:

The literature abounds in information about the oxidation of contaminants with advanced oxidation processes. Ozonation have been used for the removal of substituted phenols, Gurol et al. (1984) investigated the relation between the chemical structure of the phenolic compounds and their reactivity with ozone. They studied the ozonation of phenol respectively with p-, o- and m-hydroxylated phenols and CH₃-substituted phenols at pH 2.5. They found that due to their higher electron density in the aromatic ring, the hydroxylated phenols reacted faster than phenol. The same effect has been observed with CH₃-substituted phenols. Doré et al. (1977) have done a similar study. Ozonation has also been used to remove pesticides such 2,4-D and MCPA (Dore (1979)), Fenuron (Benitez (1991)) and other organic and inorganic compounds (Hoigné and Bader (1983)(1976); Hewes and Davison (1971)).

Ozonation is a simultaneous mass-transfer/reaction-kinetics phenomenon. Kinetic modeling of the ozonation of phenol in water has been studied by Roth et al. (1982), using a semi-empirical model which incorporate the mass transfer, resulting from the diffusional resistance of ozone, and kinetics encountered during ozonation with operating parameters for scale-up for wastewater treatment. The model is based on the following equations

$$-r_{\phi OH} = \frac{d[\phi OH]}{dt} \cdot K_n \cdot [\phi OH] \quad (1)$$

and

$$k_n = \alpha(G/V)^\beta [\phi OH]_o^\gamma [OH^-]^\delta \quad (2)$$

where:

- $-r_{\phi OH}$: global rate of phenol disappearance,
- k_n : global rate constant (mole phenol L⁻¹)¹⁻ⁿ,
- $[\phi OH]$: concentration of phenol at time t (moles.L⁻¹),
- $[\phi OH]_o$: initial concentration of phenol (moles.L⁻¹),
- $[OH^-]$: hydroxyl ion concentration (moles.L⁻¹),
- G : ozone application rate (moles.min⁻¹),
- V : liquid reaction volume (L),
- n : apparent order of phenol decomposition,
- $\alpha, \beta, \gamma, \delta$: constants determined from experimental data.

This model was applied to both semi-batch and CSTR mode operation. The versatility of the model was demonstrated by application to data of other investigators.

Photolytic ozonation:

The photolytic ozonation was also used for the oxidation of phenolic compounds. Gurol et al. (1987) studied the photolytic ozonation of mixtures of phenol, p-cresol, 2,3-xyleneol and catechol at acidic and neutral pH. The TOC removal was plotted as a function of time, during the first 100 min. TOC removal by UV light alone was negligible, by ozone 30% has been removed and more than 95% by UV/ozone. Ikemizu et al. (1987) investigated the photolytic ozonation of some aliphatic acids and alcohols, which represent the most common ozonation products, such oxalic, acetic, malonic and propionic acids and methyl and ethyl alcohols. They found that in the presence of UV radiation the initial ozonation rate of organic substances was increased by $10-10^4$ times. Photolytic ozonation was used for the oxidation of pesticides (Prado (1994)), and other organic refractory compounds (Peyton (1982, 1988); Prengle (1983)).

However, this process is still not understood from a chemical viewpoint nor is it optimized for engineering applications, but appears to be amenable to modeling. Peyton et al. (1982), proposed a formalism for the analysis of the photolytic ozonation kinetics where substrate disappearance is represented as a linear combination of terms representing purging, ozonation, photolysis and photolytic ozonation.

$$\frac{d[S]}{dt} = k_{purge}[S] + k_{photo}I^a[S]^b + k_{ozon}[O_3]_l^c[S]^d + k_{po}I^eD^f[S]^g \quad (3)$$

where I is the flux of radiation transferred into the reactor, D is the dose rate of ozone, $[O_3]_l$ is the concentration of ozone in the liquid phase, and $[S]$ is substrate concentration. In the case where rate of disappearance of substrate is a first-order process, the rate may be written as.

$$\frac{dS}{dt} = k_{tot}[S] = \sum_i k_i[S] \quad (4)$$

where k_{tot} is the pseudo-first order rate constant which represents a sum of constants for the contributing processes.

Ozone/hydrogen peroxide:

The combination of ozone and hydrogen peroxide is used essentially for the contaminants which oxidation is difficult and consumes large amounts of oxidant. Because of the high cost of ozone generation, this combination make the process economically feasible. Oxidation by combined ozone/hydrogen peroxide were used for the removal of aromatic compounds, Duguet et al. (1990) studied (at neutral pH) the ozonation of groundwater which contains several benzenic compounds, the major pollutant was o-chloronitrobenzene (70% of pollution). They found that application of 16 mg O_3/L with a 40 min contact time allows an 88% reduction of o-chloronitrobenzene, while the application of an ozone/hydrogen peroxide dosage of 8/3 during only 20 min contact time, permitted the removal of 99% of all benzenic

compounds. Ozone/hydrogen peroxide has also been used to oxidize pesticides (Beltran (1994)) and other hazardous materials (Glaze (1989); Paillard (1988)). Glaze et al. (1989) presented a model which describes the kinetics of the oxidation of substrates in water with the combination of ozone and hydrogen peroxide in a semi-batch reactor. In This model, the equation which describes the chemistry of the system is similar to that of the UV/ozone process. The rate of destruction of an organic substrate S is:

$$\frac{-d \ln[S]}{dt} = k_{sparging} + k_{S,OH}[\cdot OH] + k_{S,O_3}[O_3] \quad (5)$$

where $k_{sparging}$ is the removal rate due to the sparging and $k_{S,OH}$ and k_{S,O_3} are the second-order rate constants for the reaction of substrate with $\cdot OH$ radicals and O_3 respectively. They also studied separately the rate of ozone mass transfer and the rate of hydrogen peroxide transfer for the different substrates they studied

EXPERIMENTAL:

Experimental set up and materials:

All experiments were performed in the experimental set up shown in figure 1. The reactor is tubular with a spherical vessel with 4.54 L capacity upper. The design of this reactor possibilites the cocurrent circulation of gas (oxygen and ozone generated) and liquid (aqueous solutions of the compounds studied) which are mixed with a diffuser valve in the bottom of the reaction tube. The liquid was recirculated using a peristaltic pump.

Oxygen gas was supplied in standard cylindrical tanks and fed to an ozone generator model TDZ 11-20 TODOZONO. The saturation concentration of ozone was determined to be 1.5-2 mg/L depending on the flow rate of gas through the system. The reactor is surrounded by four low mercury lamp (15 Watts each lamp) which emit radiation at 253.7 nm.

Solutions were prepared in ultrapur water supplied by a Millipore system with a resistivity of $18 \text{ M}\Omega \cdot \text{cm}^{-1}$. For every experiment, the reactor was filled with 2500 cm^3 of aqueous solutions of analytical grade phenol or benzoic acid (from PROBUS), buffered with $0.01\text{M Na}_2\text{HPO}_4/0.01\text{M KH}_2\text{PO}_4$ to adjust the pH at 6.9. 0.05M borax buffer was used to adjust the pH of phenol solutions at 9.3 and $0.01\text{M Na}_3\text{PO}_4$ buffer to adjust the pH of benzoic acid solutions to 11.7.

analysis methods:

The samples were taken at appropriate time intervals and analysed immediately by high pressure liquid chromatography (HPLC) using a Waters chromatograph. The analyses were made in reverse phase with an ODS_2 SPHERISORB column eluting the injected sample ($20 \mu\text{L}$) with a mixture of acetonitril-water (50:50 v/v) in the case of phenol and methanol-water (60:40 v/v) with 0.5% phosphoric acid in the case of benzoic acid, with a flow rate of $1 \text{ cm}^3 \cdot \text{min}^{-1}$.

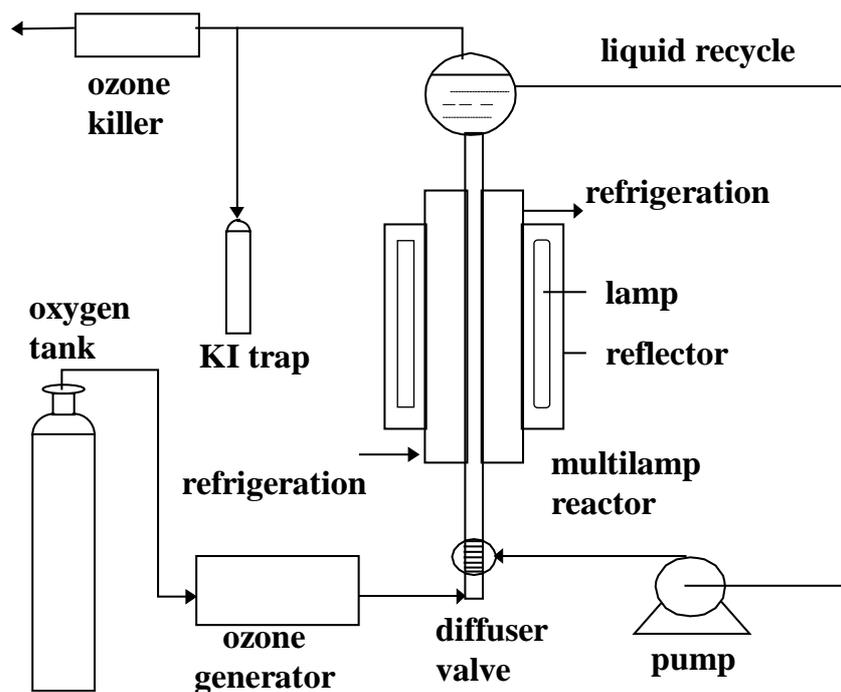


Figure 1. Experimental set-up.

For all experiments done with ozone, the excess ozone gas was passed out through the top of the reactor into a bottle containing 2% KI solution for the later iodometric determination of ozone production (Birdsall (1952)). The concentration of residual dissolved ozone was followed by the Indigo procedure (Hoigné and Bader (1983)). A spectrophotometer SHIMADZU model UV-1203 was used to measure the change in absorbance of the indigo reagent.

In addition, samples were also analysed to determine the total organic carbon (TOC), using a Dohrman DC-190 high level TOC analyser.

Operating conditions are summarized in Table I.

Table I. Experimental conditions.

Parameter	Value
Ozone production (g.h^{-1})	0.2-0.3
Intensity radiation (eins.s^{-1})	$7.22 \cdot 10^{-6}$
Gas flow rate (L.h^{-1})	60 ± 4
Liquide recirculation flow rate (L.h^{-1})	100 ± 5
Reaction volume (L)	2.5
inicial concentration phenol (mol.L^{-1})	$1.06 \pm 0.05 \cdot 10^{-3}$
Inicial concentration benzoic acid (mol.L^{-1})	$0.82 \pm 0.05 \cdot 10^{-3}$
Temperature ($^{\circ}\text{C}$)	17-25

RESULTS AND DISCUSSION:

Figures 2. and 3. show the rates of disappearance of phenol and benzoic acid at no buffered acid pH (4.9 and 2.8 respectively). As a result the pH dropped (3.2 and 2,5 respectively) due to the formation of acidic products.

Phenol concentration (mg.L⁻¹)

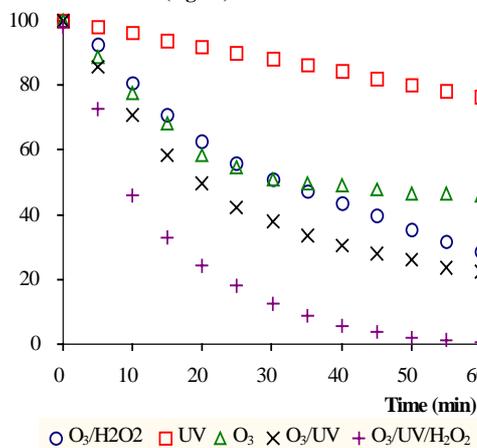


figure 2. Profiles of phenol with different AOP. pH=4.9, $[H_2O_2]_0 = 3.19 \cdot 10^{-3} \text{ mol.L}^{-1}$.

Benzoic ac concentration (mg.L⁻¹)

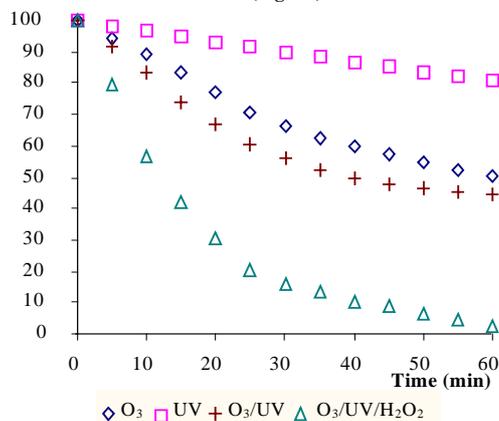
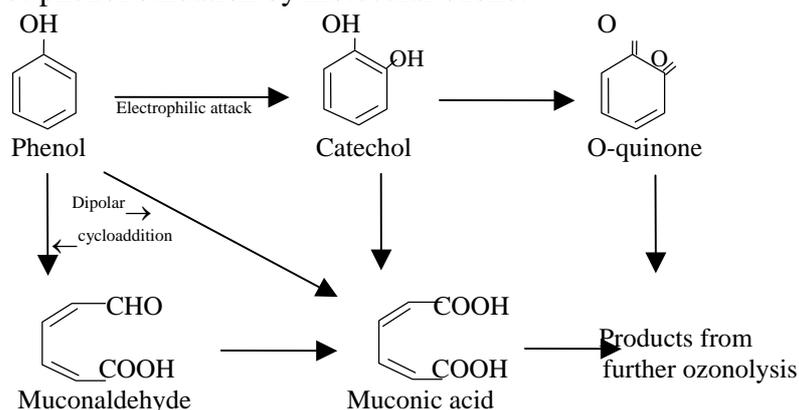


figure 3. Profiles of benzoic acid with different AOP. pH=2.8, $[H_2O_2]_0 = 3.67 \cdot 10^{-3} \text{ mol.L}^{-1}$.

Concentration profiles are similar for both compounds, phenol presents a slight increase in the amount removed for all the AOP studied. It is probably due to the fact that aromatic compounds with electron-donating groups react faster than those with electron-withdrawing group. Anyway, after 60 min ozonation, only 40-55% of benzenic compounds was removed (table II.), accordingly to the negligible rate of ozone decomposition at acid pH (Gurol and Singer (1982)) and the predominant direct reaction with molecular ozone. Ozone appeared few minutes after the beginning of all experiments with ozone (fig. 5.). Bailey et al. (1972), proposed the following mechanism of phenol oxidation by molecular ozone:



The carbons at the ortho- and para- positions to the electron-donating group (-OH) have high electron densities, thus resulting in tendency for ozone to attack at these positions. The hydroxylated phenols can also be produced by the non selective attack by $\cdot OH$ radicals; catechol, hydroquinone and benzoquinone have been identified using a $O_3/UV/H_2O_2$ process. Figure 4 shows the rate of disappearance of phenol and the rates of formation and reaction of the intermediates identified.

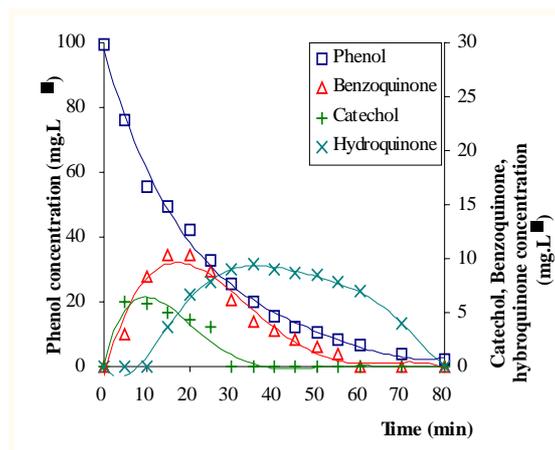


fig 4. Profiles of phenol, benzoquinone, catechol and hydroquinone. AOP: O₃/UV/H₂O₂, pH=4.9, [H₂O₂]₀=1.59.10⁻¹ mol.L⁻¹.

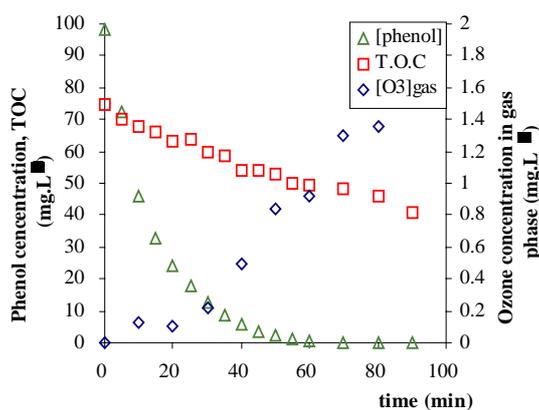


fig 5. Profiles of phenol, TOC remaining and ozone in gas phase. O₃/UV/H₂O₂, pH=4.9, [H₂O₂]₀=6.37.10⁻² mol.L⁻¹.

Whereas for benzoic acid, the initial attack of ozone molecule is usually at the activated meta- position to the electron-withdrawing group (-COOH) (Masten (1994)). No bibliography was found describing the ozonation of benzoic acid. Ogata et al. (1980) studied the photo-oxidation of benzoic acid in combination with H₂O₂, they expected that hydroxylation of the aromatic ring by ·OH radicals would compete with decarbonylation or decarboxylation of benzoic acid. They also identified hydroxybenzoic acids, phenol and benzene as reaction intermediates, which are found to be more reactive than benzoic acid itself towards the ·OH radical.

Table II. Experiments at acidic pH.

AOP	[H ₂ O ₂] ₀ (mol/L)	ΦOH ₆₀ removed (%)	[H ₂ O ₂] ₀ (mol/L)	ΦCOOH ₆₀ removed (%)
UV	-	23.6	-	23.5
O ₃	-	54.2	-	49.7
O ₃ /UV	-	77.4	-	55.4
O ₃ /H ₂ O ₂	6.37.10 ⁻²	71.2	-	-
O ₃ /UV/H ₂ O ₂	3.19.10 ⁻³	89.5	1.47.10 ⁻⁴	85.5
O ₃ /UV/H ₂ O ₂	7.44.10 ⁻³	93.2	3.67.10 ⁻⁴	97.2
O ₃ /UV/H ₂ O ₂	1.27.10 ⁻²	94.7	-	-
O ₃ /UV/H ₂ O ₂	3.18.10 ⁻²	98.0	-	-
O ₃ /UV/H ₂ O ₂	6.37.10 ⁻²	99.4	-	-
O ₃ /UV/H ₂ O ₂	9.53.10 ⁻²	95.1	-	-

$O_3/UV/H_2O_2$	$1.27 \cdot 10^{-1}$	97.0
$O_3/UV/H_2O_2$	$1.59 \cdot 10^{-1}$	93.2

ΦOH_{60} : pourcentage of phenol removed after 60 min reaction time.

$\Phi COOH_{60}$: pourcentage of benzoic acid removed after 60 min reaction time.

Figure 5. shows the TOC removal and ozone concentration in gas phase as a function of time of photolytic ozonation combined with hydrogen peroxide which has been found to be more effective at acid pH. Influence of initial H_2O_2 concentration have been studied in the case of phenol, 9 experiments were carried out with different initial concentrations of H_2O_2 (table II.). It can be seen that the oxidation rate of phenol first increases when hydrogen peroxide concentration increases, the opposite effect was observed at high concentrations of H_2O_2 . $63.7 \cdot 10^{-3}$ mol/L was found to be the optimal concentration and correspond to the removal of all phenol and 40% TOC after 70 min reaction time (figure 5.).

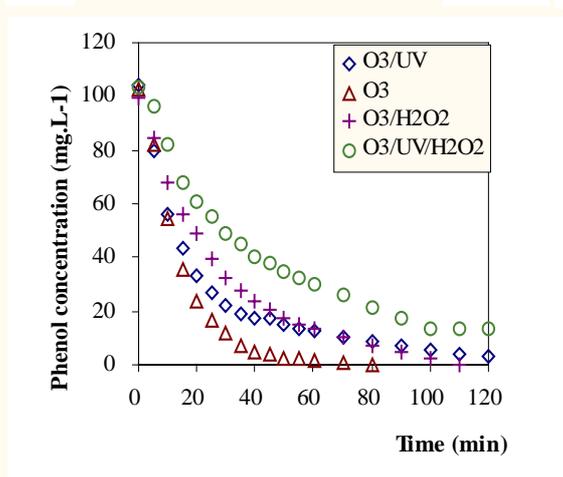
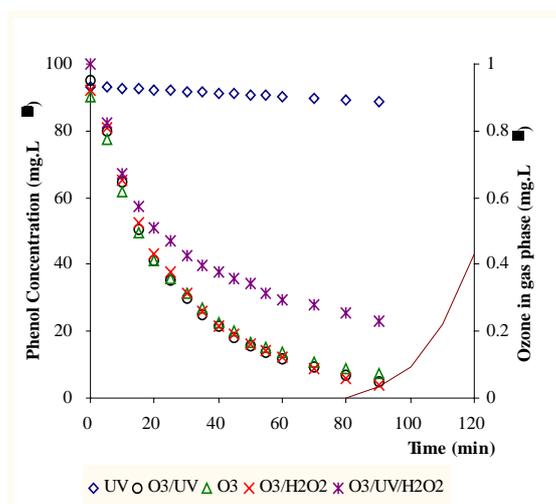


Figure 6. Profiles of phenol with different AOP.

— ozone in gas phase. pH=6.8-7.2,
 $[H_2O_2]_0 = 0.58 \cdot 10^{-3}$ mol.L⁻¹.

Figure 7. profiles of phenol with different AOP. pH=9.3-9.5, $[H_2O_2]_0 = 0.58 \cdot 10^{-3}$ mol.L⁻¹.

Similar experiments were carried out at pH 6.9-7.2, phenol removal by ozonation have increased as found by Singer and Gurol (1983), the same result was observed for benzoic acid. However, against what we had expected, the removal rates of phenol were almost the same for all the AOP experimented (fig 5.), where the TOC removed was about 35-40%, except UV alone where the amount of phenol removed was

negligible. Table III. shows the pourcentages of phenol removed after 60 and 90 min reaction time for each experiment.

Table III. Experiments with phenol at neutral pH (6.8-7.2) and basic pH (9.3-9.5)

AOP	[H ₂ O ₂] ₀ (mol/L)	PhOH ₆₀ removed at pH _{neut} (%)	PhOH ₉₀ removed at pH _{neut} (%)	PhOH ₆₀ removed at pH _{bas} (%)	PhOH ₉₀ removed at pH _{bas} (%)
UV	-	5.6	8		
O ₃	-	84.8	92.1	98.7	100
O ₃ /UV	-	87.7	94.6	88.2	93.5
O ₃ /H ₂ O ₂	0.58 · 10 ⁻⁴	84.8	92.8		
O ₃ /H ₂ O ₂	0.58 · 10 ⁻³	86.6	95.8	86.3	95.0
O ₃ /H ₂ O ₂	2.94 · 10 ⁻³	79.4	89.8	80.5	92.5
O ₃ /H ₂ O ₂	7.35 · 10 ⁻³	78.9	89.5		
O ₃ /H ₂ O ₂	1.47 · 10 ⁻²	70.3	80.9		
O ₃ /UV/H ₂ O ₂	0.58 · 10 ⁻³	70.5	76.9	70.9	83.6

This results show that at neutral pH, hydrogen peroxide has a slight influence in the rate of phenol ozonation. However, it has a scavenging effect in the case of photolytic ozonation. It can be accepted that at this pH ozone decomposition starts to be important. Ozone hasn't been detected until all phenol was almost completely oxidized after 90-100 min reaction time (fig. 5.)

The results of the experiments done at basic pH (9.3-9.5) are shown in table III. The rate of phenol decomposition increased considerably in the case of ozonation which has been found to be more effective. No ozone has been detected even if all phenol was removed. This can be explained by the predominance of direct attack by free radicals which is fast and less selective compared to the direct oxidation by ozone and leads to the formation of unidentified intermediates and products.

CONCLUSIONS:

All the Advanced Oxidation Processes used in this work yield to the removal of the compounds studied, but with different reaction rates.

The pH is an important variable to take into account. At acid pH, the direct attack by molecular ozone is predominant and any source of radicals (H₂O₂ or/and UV) improve the efficiency of ozonation, while at neutral and basic pH there is a major contribution of the free-radical pathway and the addition of hydrogen peroxide and/or UV can promote or inhibit the reaction of ozonation.

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REFERENCES:

- Bailey, P. S. (1972). Reactivity of ozone with various organic functional groups important to water purification. Ozone in water and wastewater treatment. Chap 3. Edited by Evans F. L.
- Beltran, F. J., et al. (1994). Oxidation of mecoprop in water with ozone and ozone combined with hydrogen peroxide. *Ind. Eng. Chem. Res.*, 33, 125-136.
- Benitez, F. J. et al. (1991). Ozonation of aqueous solutions of Fenuron. *Ind. Eng. Chem. Res.*, 30, 2390-2395.
- Birdsall, C. M. et al. (1952). Iodometric determination of ozone. *Anal. Chem.* 24(4), 662-664.
- Doré, M. et al. (1977). Ozonation des phenols et des acides phenoxyacetiques. *Wat. Res.*, 12, 143-425.
- Doré, M. et al. (1979). Mecanisme de l'ozonation des herbicides derivés de l'acide phenoxyacetique: 2,4-D et MCPA. *Wat. Res.*, 14, 767-773.
- Duguet, J. P. et al. (1990). Application of combined ozone-hydrogen peroxide for the removal of aromatic compounds from groundwater. *Ozone. Scien. Eng.*, 12(3), 281-293.
- Glaze, W. H. and Kang, J-W. (1989). Advanced oxidation processes. Test of a kinetic model for the oxidation of organics... *Ind. Eng. Chem. Res.*, 28(11), 1580-1587.
- Gurol, M. D. and Singer, P. C. (1982). Kinetics of ozone decomposition: a dynamic approach. *Environ. Sci. Technol.*, 16(7), 377-383.
- Gurol, M. D. et al. (1984). Kinetic behavior of ozone in aqueous solutions of substituted phenols. *Ind. Eng. Chem. Fundam.*, 23(1), 54-60.
- Gurol, M. D. and Vastistas, R. (1987). Oxidation of phenolic compounds by ozone and ozone+uv radiation: a comparative study. *Wat Res.*, 21(8), 895-900.
- Hewes, C. G. and Davison, R. R. (1971). Kinetics of ozone decomposition and reaction with organics in water. *AIChE. Journal.*, 17(1), 141-147.
- Hoigné, J. and Bader, H. (1976). The role of hydroxyl radical reactions in ozonation process in aqueous solutions. *Wat. Res.*, 10, 377-386.
- Hoigné, J. and Bader, H. (1983). Rate constants of reactions of ozone with organic and inorganic compounds in water. *Wat. Res.*, 17, 173-183.
- Ikemizu, K. et al. (1987). Ozonation of organic refractory compounds in water in combination with UV radiation. *J. Chem. Eng. Japan.*, 20(4), 369-374.
- Masten, S. J. and Davies, S. H. R. (1994). The use of ozonation to degrade organic contaminants in wastewaters. *Environ. Sci. Tech.*, 28(4), 180A-185A.
- Ogata, Y. et al. (1980). Photoinduced oxidation of benzoic acid with aqueous hydrogen peroxide. *J. C. S. Perkin II*, 616-619.
- Paillard, H. et al. (1988). Optimal conditions for applying an ozone-hydrogen peroxide oxidizing system. *Wat. Res.*, 22(1), 91-103.
- Peyton, G. R. et al. (1982). Destruction of pollutants in water with ozone in combination with Ultraviolet radiation: 1, 2. *Environ. Sci. Technol.*, 16(8), 448-453.
- Peyton, G. R. and Glaze, W. H. (1988). Destruction of pollutants in water with ozone in combination with Ultraviolet radiation: 3. *Environ. Sci. Technol.*, 22, 761-767.
- Prado, J. et al. (1994). Degradation of 2,4-D by ozone and light. *Ozone Scien. Eng.*, 16, 235-246.

- Prengle, H. W. Jr. et al. (1983). Experimental rate constants and reactor considerations for the destruction of micropollutants and trihalomethane precursors by ozone with UV radiation. *Envir. Scien. Tech.*, 17, 743-747.
- Roth, J. A. et al. (1982). Kinetic modeling of ozonation of phenol in water. *Journal WPCF.*, 54(1), 135-138.
- Singer, P. C. and Gurol, M. D. (1983). Dynamics of the ozonation of phenol -I. *Wat. Res.*, 17(9), 1163-1181.